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(54) METHOD FOR PRODUCING CROSS-LINKED POLYELECTROLYTE AND CROSS-LINKED POLYELECTROLYTE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cross-linked polyelectrolyte having excellent permanency and useful as a proton conductive membrane such as an electrolyte for primary batteries, an electrolyte for secondary batteries, a solid polyelectrolyte for fuel cells, a display element, various kinds of sensors, a signal transmission medium, a solid capacitor or an ion exchange membrane while maintaining essentially possessed high proton conductivity.

SOLUTION: This cross-linked polyelectrolyte having a high cross-linking density is produced by subjecting a monomer having at least ≥2 radically polymerizable groups in one molecule to a polymerizing reaction in the presence of a proton conductive polymer.

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[Date of final disposal for application]

[Patent number]

[Date of registration]

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* NOTICES *

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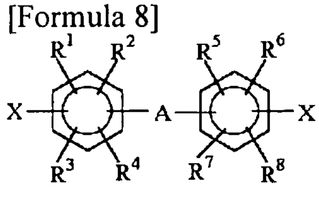
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the high endurance solid-state polyelectrolyte excellent in the oxidation resistance used in more detail suitable for solid-state polyelectrolyte film, such as a polyelectrolyte mold fuel cell and a water electrolysis cel, etc., and its process about a high endurance solid-state polyelectrolyte.
[0002]
[Description of the Prior Art] Solid-state polyelectrolytes are solid-state polymeric materials which have electrolyte radicals, such as a sulfonic group and a carboxylic-acid radical, in a giant-molecule chain, and since it combines with specific ion firmly or has the property which penetrates a cation or an anion alternatively, they are used as polyelectrolyte film in a polyelectrolyte mold fuel cell or a water electrolysis cel.
[0003] A polyelectrolyte mold fuel cell prepares the electrode of a pair in both sides of the solid-state polyelectrolyte film of proton conductivity, supplies it to one electrode (fuel electrode) by making pure hydrogen or reforming hydrogen gas into fuel gas, supplies oxygen gas or air to a different electrode (air pole) as an oxidizer, and acquires electromotive force. Moreover, by electrolyzing water using the solid-state polyelectrolyte film, the reverse reaction of a fuel cell reaction occurs and water electrolysis manufactures hydrogen and oxygen.
[0004] However, in an actual fuel cell and water electrolysis, the side reaction other than these main reactions occurs. The typical thing is generation of a hydrogen peroxide (H2O2). The oxygen currently mixed by mixing intentionally as an impurity into gas or the oxygen which melted into the electrolyte on the oxygen pole and has been diffused to the hydrogen pole is considered to participate in a reaction by generation of this hydrogen peroxide (H2O2), and the side reaction to which water electrolysis, on the other hand, generates a hydrogen peroxide (H2O2) almost similarly may occur in it on the hydrogen pole.
[0005] And the hydrogen peroxide generated on these electrodes deserts an electrode by diffusion etc., and moves into an electrolyte. Since this hydrogen peroxide is the strong matter of oxidizing power, it oxidizes many organic substance which constitutes an electrolyte. Although the detailed mechanism is not necessarily clear, in many cases, a hydrogen peroxide is considered that it radical-izes and the generated hydrogen-peroxide radical has become the direct reacting matter of oxidation reaction.
[0006] In JP,2001-118591,A, in order to raise the endurance of a polyelectrolyte, the high endurance polyelectrolyte excellent in the oxidation resistance over the peroxide generated by the cell reaction is indicated. In this official report, even if there are whether distributed combination of the peroxide stabilizers, such as a metal peroxide which carries out distributed combination of the transition-metals oxide which has the catalyst ability which specifically cracks a peroxide catalytically in a polyelectrolyte, or controls disassembly of a peroxide, is carried out, or a phenolic hydroxyl group is introduced [little] into an electrolyte macromolecule by the chemical bond, one of means is taken. However, if a metal peroxide is blended into a polyelectrolyte, since film reinforcement will fall extremely, the serious trouble that the macromolecule electrolysis film is torn at the time of the installation at the time of actually creating a fuel cell using the macromolecule electrolysis film etc. occurs. Moreover, very many phenolic hydroxyl groups needed to be introduced to discover high radical resistance by the approach of introducing a phenolic hydroxyl group into an electrolyte giant molecule by the chemical bond, and since the fatal problem to which the proton conductivity of a polyelectrolyte falls occurred, maintaining high proton conductivity, the approach of maintaining high radical resistance and tough film reinforcement had a limitation, and was still inadequate.
[0007]
[Problem(s) to be Solved by the Invention] This invention aims at offering the polyelectrolyte excellent in permanency, maintaining the high proton conductivity which it originally has.

[0008]
[Means for Solving the Problem] This invention relates to the approach of carrying out the polymerization reaction of the monomer which has at least two or more radical polymerization nature machines in 1 molecule, and manufacturing a crosslinked polymer electrolyte under existence of a proton conductivity polymer in order to solve the above-mentioned technical problem. Moreover, it is related with the crosslinked polymer electrolyte itself which was obtained by this manufacture approach and whose insoluble matter to N-methyl pyrrolidone is 40 % of the weight or more.
[0009] 1. [a proton conductivity polymer]
A proton conductivity polymer has an electrolyte radical and the hydrocarbon section, and ion plasticity functional groups, such as a sulfonic group and a carboxylic-acid radical, are mentioned as an electrolyte radical. Furthermore, said electrolyte radical is introduced into the hydrocarbon section of a proton conductivity polymer at the predetermined rate of installation to the part which can introduce an electrolyte radical.
[0010] As an example of a high molecular compound of having the hydrocarbon section into which the above-mentioned electrolyte radical is introduced Poly arylene sulfone resin, polyether sulphone resin, polyether ether ketone resin, Straight chain mold phenol-formaldehyde resin, bridge formation mold phenol formaldehyde resin, Straight chain mold polystyrene resin, bridge formation mold polystyrene resin, straight chain mold Pori (trifluoro styrene) resin, Bridge formation mold (trifluoro styrene) resin, Pori (2, 3-diphenyl -1, 4-phenylene oxide) resin, Pori (allyl compound ether ketone) resin, Pori (arylene ether sulfone) resin, Pori (phenyl kino SANRIN) resin, Pori (benzyl silane) resin, polystyrene-graft-ethylene tetrafluoroethylene resin, polystyrene-graft-polyvinylidene fluoride resin, polystyrene-graft-tetrafluoroethylene resin, etc. are mentioned.
[0011] In this invention, sulfonation poly arylene is preferably used as a proton conductivity polymer. Moreover, when it has a radical reaction nature machine in a proton conductivity polymer, since a crosslinked polymer electrolyte with much insoluble matter of N-methyl pyrrolidone is obtained at least, the amount of the monomer used which has at least two or more radical polymerization nature machines in 1 molecule used by this invention is desirable. The alkyl group (example: isopropyl group) which has the 3rd class carbon by which a hydrogen atom is easily drawn out with a free radical as this radical reaction nature machine, an aryl group, a vinyl group, a sulfhydryl group, an acryloyl radical, a methacryloyl radical, etc. can be mentioned. Especially in the case of the alkyl group which has the 3rd class carbon, since the crosslinked polymer electrolyte which this functional group acted efficiently as a crosslinking reaction point, and constructed the bridge over altitude more since the alkyl group which has the 3rd class carbon of this tends to have remained in a polymer is obtained, after sulfonation is desirable.
[0012] Since it has flexibility structure by the above-mentioned unit (A) that it is the poly arylene system polymer which includes the aromatic compound unit (henceforth a unit (A)) which has an electronic suction nature machine in the (a) principal chain as poly arylene before a sulfonation reaction in a principal chain, toughness is high and desirable.
[0013] Moreover, since toughness and hot water resistance cannot fall easily and it excels in toughness, a mechanical strength, an elastic modulus, and anti-bloating tendency even if that it is the poly arylene system copolymer including the above-mentioned unit (A) and the aromatic compound unit (henceforth a unit (B)) which does not have an electronic suction nature machine in the (b) principal chain can control the amount of introductory upper limits of a sulfonic group by the unit (B) and it sulfonates, it is this better ** more.
[0014] (1) As a monomer (henceforth "a monomer (A)") which constitutes the monomeric unit (A) which constitutes a unit (A), the following general formula (a1-1m) and (a1-2m) (a2m) the thing monomer (henceforth "a monomer (A1)", "a monomer (A2)", and "a monomer (A3)" in order of) expressed are mentioned preferably.
[0015]
[Formula 8]

-- (a1-1m)
(X is a chlorine atom, a bromine atom, an iodine atom, or -OSO2Y (it is here and Y shows an alkyl group, an alkyl halide radical, or an aryl group) independently among a general formula (a1-1m), and A is an electronic suction nature machine and is that R1-R8 are the same or a difference, a hydrogen atom, a fluorine atom, an allyl group, an alkyl group, or a fluoro alkyl group.)
[0016] As an electronic suction nature machine (A), -CO-, -CONH-, -(CF2) p- (it is here and p is the integer of 1-10), -C(CF3)2-, -COO-, -SO-, -SO2-, etc. are mentioned among the above-mentioned general formula (a1-

1m).

[0017] Similarly, as the above-mentioned alkyl group, a methyl group, an ethyl group, an isopropyl group, etc. are mentioned, and a trifluoromethyl radical, a pentafluoro ethyl group, etc. are mentioned as a fluoro alkyl group. Since it acts as a point in the case of crosslinking reaction constructing a bridge and crosslinking reaction occurs efficiently, the isopropyl group which has the 3rd class carbon is this better **.

[0018] Similarly, if referred to as Z in -OSO2Y, as an alkyl group, a trifluoromethyl radical, a pentafluoro ethyl group, etc. are mentioned as an alkyl halide radical, and a methyl group, an ethyl group, etc. are mentioned for a phenyl group, p-tolyl group, etc. as an aryl group.

[0019] The example of the above-mentioned monomer (A1) is shown in a degree. A - dichloro benzophenone, and 4 and 4 '2, 4'-dichloro benzophenone, (A1-1) A - dichloro benzophenone, and 3 and 3 '4, 4'-dibromo benzophenone, 2, a - dibromo benzophenone, and 4 '3, 3'-dibromo benzophenone, A 4 and 4'-diiodo benzophenone, 2, a - diiodo benzophenone, and 4 '3, 3'-diiodo benzophenone, a bis(4-trifluoromethyl sulfo NIROKISHI phenyl) ketone, a bis(3-trifluoromethyl sulfo NIROKISHI phenyl) ketone.

[0020] (A1-2) - diiodo benzanilide, and - dibromo benzanilide, and - dichloro benzanilide, and 4 and 4'-dichloro benzanilide, 3, and 3 '3, 4'-dichloro benzanilide, 4, and 4 '3, 3'-dibromo benzanilide, 3, - dibromo benzanilide, and 4 '4, 4'-diiodo benzanilide, 3, and 3 '3, 4'-diiodo benzanilide.

[0021] (A1-3) Bis(chlorophenyl) difluoromethane, bis(chlorophenyl) tetrafluoro ethane, Bis(chlorophenyl) hexafluoropropane, bis(chlorophenyl) octafluoro butane, A bis(chlorophenyl) deca fluoro pentane, a bis (chlorophenyl) dodeca fluoro hexane, A bis(chlorophenyl) tetra-deca fluoro heptane, a bis(chlorophenyl) hexa deca fluoro octane, A bis(chlorophenyl) OKUTA deca fluoro nonane, a bis(chlorophenyl) eicosa fluoro decane, Bis(BUROMO phenyl) difluoromethane, bis(BUROMO phenyl) tetrafluoro ethane, Bis(BUROMO phenyl) hexafluoropropane, bis(BUROMO phenyl) octafluoro butane, A bis(BUROMO phenyl) deca fluoro pentane, a bis(BUROMO phenyl) dodeca fluoro hexane, A bis(BUROMO phenyl) tetra-deca fluoro heptane, a bis (BUROMO phenyl) hexa deca fluoro octane, A bis(BUROMO phenyl) OKUTA deca fluoro nonane, a bis (BUROMO phenyl) eicosa fluoro decane, Bis(iodine phenyl) difluoromethane, bis(iodine phenyl) tetrafluoro ethane, Bis(iodine phenyl) hexafluoropropane, bis(iodine phenyl) octafluoro butane, A bis(iodine phenyl) deca fluoro pentane, a bis(iodine phenyl) dodeca fluoro hexane, A bis(iodine phenyl) tetra-deca fluoro heptane, a bis (iodine phenyl) hexa deca fluoro octane, a bis(iodine phenyl) OKUTA deca fluoro nonane, a bis(iodine phenyl) eicosa fluoro decane.

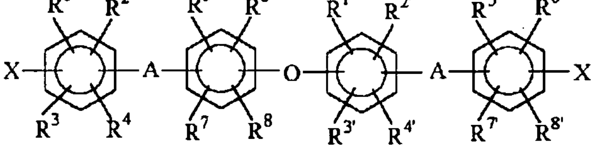
[0022] 2 and 2-bis(4-chlorophenyl) hexafluoropropane, (A1-4) 2 and 2-bis(3-chlorophenyl) hexafluoropropane, 2, and 2-bis(4-BUROMO phenyl) hexafluoropropane, 2 and 2-bis(3-BUROMO phenyl) hexafluoropropane, 2, and 2-bis(4-iodine phenyl) hexafluoropropane, 2 and 2-bis(3-iodine phenyl) hexafluoropropane, bis(4-trifluoromethyl sulfo NIROKISHI phenyl) hexafluoropropane, bis(3-trifluoromethyl sulfo NIROKISHI phenyl) hexafluoropropane.

[0023] 4-chloro benzoic-acid-4-chlorophenyl, 4-chloro benzoic-acid-3-chlorophenyl, (A1-5) 3-chloro benzoic-acid-3-chlorophenyl, 3-chloro benzoic-acid-4-chlorophenyl, 4-BUROMO benzoic-acid-4-BUROMO phenyl, 4-BUROMO benzoic-acid-3-BUROMO phenyl, 3-BUROMO benzoic-acid-3-BUROMO phenyl and 3-BUROMO benzoic-acid-4-BUROMO phenyl (A1-6) Bis(4-chlorophenyl) sulfoxide, A bis(3-chlorophenyl) sulfoxide, a bis(4-BUROMO phenyl) sulfoxide, A bis(3-BUROMO phenyl) sulfoxide, a bis(4-iodine phenyl) sulfoxide, A bis(3-iodine phenyl) sulfoxide, a bis(4-trifluoromethyl sulfo NIROKISHI phenyl) sulfoxide, a bis (3-trifluoromethyl sulfo NIROKISHI phenyl) sulfoxide.

[0024] (A1-7) A bis(4-chlorophenyl) sulfone, a bis(3-chlorophenyl) sulfone, a bis(4-BUROMO phenyl) sulfone, a bis(3-BUROMO phenyl) sulfone, a bis(4-iodine phenyl) sulfone, a bis(3-iodine phenyl) sulfone, a bis (4-trifluoromethyl sulfo NIROKISHI phenyl) sulfone, bis(3-trifluoromethyl sulfo NIROKISHI phenyl) sulfone.

[0025]

[Formula 9]



-- (al-2m)

(X, R1-R8 are as having defined the formula (al-1m) among a general formula (al-2m), A is an electronic suction nature machine as the formula (al-1m) was defined independently, and R1' - R8' is the same -- or it differs and they are a hydrogen atom, a fluorine atom, an allyl group, an alkyl group, or a fluoro alkyl group.) It is a thing as the general formula (al-1m) was defined as the alkyl group in the above-mentioned general formula (al-2m), and a fluoro alkyl group.

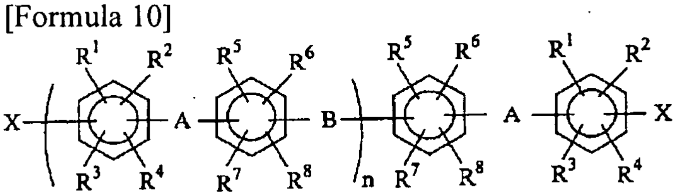
[0026] The example of the above-mentioned monomer (A2) is shown in a degree. 4 and 4'-bis(4-chloro benzoyl) diphenyl ether, (A2-1) - bis(3-chloro benzoyl) diphenyl ether, and 4 and 4 '4, 4'-bis(4-BUROMO benzoyl) diphenyl ether, - bis(3-BUROMO benzoyl) diphenyl ether, and 4 and 4 '4, 4'-bis(4-iodine benzoyl) diphenyl ether, - bis(3-iodine benzoyl) diphenyl ether, and 4 and 4 '4, 4'-bis(4-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether, - bis(4-methyl sulfo NIROKISHI phenyl) diphenyl ether, and 4 and 4'-bis (3-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether, 4, and 4 '4, 4'-bis(3-methyl sulfo NIROKISHI phenyl) diphenyl ether.

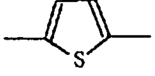
[0027] 4 and 4'-bis(4-chlorobenzo ylamino) diphenyl ether, (A2-2) 3, 4'-bis(4-chloro benzoyl friend) diphenyl ether, 4 and 4'-bis(3-chlorobenzo ylamino) diphenyl ether, 3, - bis(3-chloro benzoyl) diphenyl ether, and 4 '4, 4'-bis(4-bromobenzo ylamino) diphenyl ether, 3, 4'-bis(4-bromobenzo ylamino) diphenyl ether, 4 and 4'-bis(3-bromobenzo ylamino) diphenyl ether, 3, 4'-bis(3-bromobenzo ylamino) diphenyl ether, 4 and 4'-bis(4-iodine benzoylamino) diphenyl ether, 3, 4'-bis(4-iodine benzoylamino) diphenyl ether, 4 and 4'-bis(3-iodine benzoylamino) diphenyl ether, 3, 4'-bis(3-iodine benzoylamino) diphenyl ether, 4 and 4'-bis(4-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether, 3, 4'-bis(4-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether, 4 and 4'-bis(3-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether, 3, 4'-bis(3-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether, 4 and 4'-bis(4-methyl sulfo NIROKISHI phenyl) diphenyl ether, - bis(3-methyl sulfo NIROKISHI phenyl) diphenyl ether, and 3, 4'-bis(4-methyl sulfo NIROKISHI phenyl) diphenyl ether, 4, and 4 '3, 4'-bis(3-methyl sulfo NIROKISHI phenyl) diphenyl ether.

[0028] 4 and 4'-bis(4-chlorophenyl sulfonyl) diphenyl ether, (A2-3) 3, 4'-bis(4-chlorophenyl sulfonyl) diphenyl ether, 4 and 4'-bis(3-chlorophenyl sulfonyl) diphenyl ether, 3, 4'-bis(3-chlorophenyl sulfonyl) diphenyl ether, 4 and 4'-bis(4-BUROMO phenyl sulfonyl) diphenyl ether, 3, 4'-bis(4-BUROMO phenyl sulfonyl) diphenyl ether, 4 and 4'-bis(3-BUROMO phenyl sulfonyl) diphenyl ether, 3, 4'-bis(3-BUROMO phenyl sulfonyl) diphenyl ether, 4 and 4-bis(4-iodine phenyl sulfonyl) diphenyl ether, 3, 4'-bis(4-iodine phenyl sulfonyl) diphenyl ether, 4 and 4'-bis(3-iodine phenyl sulfonyl) diphenyl ether, 3, 4'-bis(3-iodine phenyl sulfonyl) diphenyl ether, 4 and 4'-bis(4-trifluoromethyl sulfo NIROKISHIFENI sulfonyl) diphenyl ether, 3, 4'-bis(4-trifluoromethyl sulfo NIROKISHIFENIRU sulfonyl) diphenyl ether, 4 and 4'-bis(3-trifluoromethyl sulfo NIROKISHIFENI sulfonyl) diphenyl ether, 3, 4'-bis(3-trifluoromethyl sulfo NIROKISHIFENIRU sulfonyl) diphenyl ether, 4 and 4'-bis(4-methyl sulfo NIROKISHIFENI sulfonyl) diphenyl ether, 3, 4'-bis(4-methyl sulfo NIROKISHIFENIRU sulfonyl) diphenyl ether, - bis(3-methyl sulfo NIROKISHIFENI sulfonyl) diphenyl ether, and 4 and 4 '3, 4'-bis (3-methyl sulfo NIROKISHIFENIRU sulfonyl) diphenyl ether.

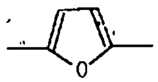
[0029] A 4 and 4'-bis(4-chlorophenyl) diphenyl ether dicarboxy rate, (A2-4) 3, a 4'-bis(4-chlorophenyl) diphenyl ether dicarboxy rate, A 4 and 4'-bis(3-chlorophenyl) diphenyl ether dicarboxy rate, 3, a 4'-bis(3-chlorophenyl) diphenyl ether dicarboxy rate, A 4 and 4'-bis(4-BUROMO phenyl) diphenyl ether dicarboxy rate, 3, a 4'-bis(4-BUROMO phenyl) diphenyl ether dicarboxy rate, A 4 and 4'-bis(3-BUROMO phenyl) diphenyl ether dicarboxy rate, 3, a 4'-bis(3-BUROMO phenyl) diphenyl ether dicarboxy rate, A 4 and 4'-bis(4-iodine phenyl) diphenyl ether dicarboxy rate, 3, a 4'-bis(4-iodine phenyl) diphenyl ether dicarboxy rate, A 4 and 4'-bis (3-iodine phenyl) diphenyl ether dicarboxy rate, 3, a 4'-bis(3-iodine phenyl) diphenyl ether dicarboxy rate, A 4 and 4'-bis(4-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether dicarboxy rate, 3, a 4'-bis(4-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether dicarboxy rate, A 4 and 4'-bis(3-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether dicarboxy rate, 3, a 4'-bis(3-trifluoromethyl sulfo NIROKISHI phenyl) diphenyl ether dicarboxy rate, A 4 and 4'-bis(4-methyl sulfo NIROKISHI phenyl) diphenyl ether dicarboxy rate, 3, a 4'-bis(4-methyl sulfo NIROKISHI phenyl) diphenyl ether dicarboxy rate, - bis(3-methyl sulfo NIROKISHI phenyl) diphenyl ether dicarboxy rate, and 4 and 4 '3, 4'-bis(3-methyl sulfo NIROKISHI phenyl) diphenyl ether dicarboxy rate.

[0030] 4 and 4' bis[-] [(4-chlorophenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, (A2-5) 3, 4' bis[-] [(4-chlorophenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-chlorophenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 3, 4' bis[-] [(3-chlorophenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 4, 4'-screw [(4-BUROMO phenyl)-1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 3, 4' bis[-] [(4-BUROMO phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-BUROMO phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 3, 4' bis[-] [(3-BUROMO phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(4-iodine phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 3, 4' bis[-] [(4-iodine phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-iodine phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 3, 4' bis[-] [(3-iodine phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(4-trifluoromethyl sulfo NIROKISHI phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 3, 4' bis[-] [(4-trifluoromethyl sulfo NIROKISHI phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-trifluoromethyl sulfo NIROKISHI phenyl)

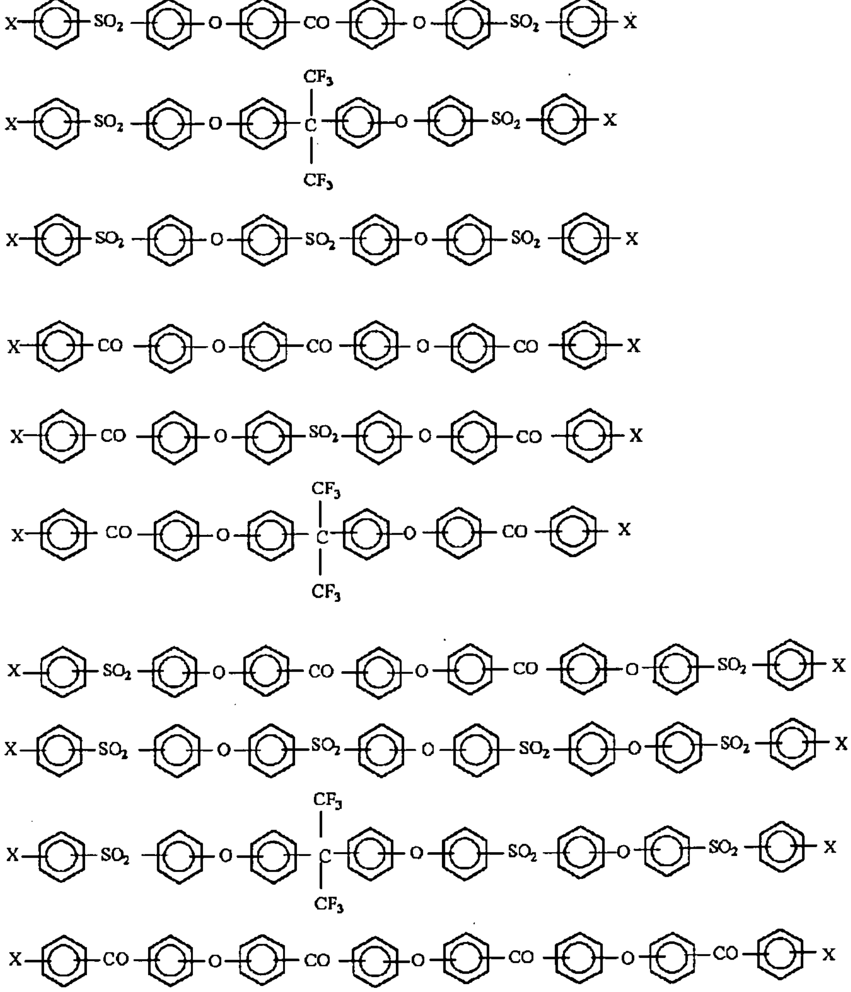
-1, 1, 1; 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 3, 4' bis[-] [(3-trifluoromethyl sulfo NIROKISHI phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(4-methyl sulfo NIROKISHI phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 3, 4' bis[-] [(4-methyl sulfo NIROKISHI phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-methyl sulfo NIROKISHI phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether, 3 and 4' bis[-] [(3-methyl sulfo NIROKISHI phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoro propyl] diphenyl ether.
[0031] 4 and 4' bis[-] [(4-chlorophenyl) tetrafluoro ethyl] diphenyl ether, (A2-6) 4 and 4' bis[(3-chlorophenyl) tetrafluoro ethyl] diphenyl ether, 4 and 4' bis[-] [(4-chlorophenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-chlorophenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[(4-chlorophenyl) octafluoro butyl] diphenyl ether, 4 and 4' bis[-] [(3-chlorophenyl) octafluoro butyl] diphenyl ether, 4 and 4' bis[-] [(4-chlorophenyl) deca fluoro pentyl] diphenyl ether, 4 and 4' bis[-] [(3-chlorophenyl) deca fluoro pentyl] diphenyl ether, 4 and 4' bis[-] [(4-BUROMO phenyl) tetrafluoro ethyl] diphenyl ether, 4 and 4' bis[-] [(3-BUROMO phenyl) tetrafluoro ethyl] diphenyl ether, 4 and 4' bis[-] [(4-BUROMO phenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-BUROMO phenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(4-BUROMO phenyl) octafluoro butyl] diphenyl ether, 4 and 4' bis[-] [(3-BUROMO phenyl) octafluoro butyl] diphenyl ether, 4 and 4' bis[-] [(4-BUROMO phenyl) deca fluoro pentyl] diphenyl ether, 4 and 4' bis[-] [(3-BUROMO phenyl) deca fluoro pentyl] diphenyl ether, 4 and 4' bis[-] [(4-iodine phenyl) tetrafluoro ethyl] diphenyl ether, 4 and 4' bis[-] [(3-iodine phenyl) tetrafluoro ethyl] diphenyl ether, 4 and 4' bis[-] [(4-iodine phenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-iodine phenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(4-iodine phenyl) octafluoro butyl] diphenyl ether, 4 and 4' bis[-] [(3-iodine phenyl) octafluoro butyl] diphenyl ether, 4 and 4' bis[-] [(4-iodine phenyl) deca fluoro pentyl] diphenyl ether, 4 and 4' bis[-] [(3-iodine phenyl) deca fluoro pentyl] diphenyl ether, 4 and 4' bis[-] [(4-trifluoromethyl sulfo NIROKISHI phenyl) tetrafluoro ethyl] diphenyl ether, 4 and 4' bis[-] [(3-trifluoromethyl sulfo NIROKISHI phenyl) tetrafluoro ethyl] diphenyl ether, 4 and 4' bis[-] [(4-trifluoromethyl sulfo NIROKISHI phenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-trifluoromethyl sulfo NIROKISHI phenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(4-trifluoromethyl sulfo NIROKISHI phenyl) octafluoro butyl] diphenyl ether, 4 and 4' bis[-] [(3-trifluoromethyl sulfo NIROKISHI phenyl) octafluoro butyl] diphenyl ether, 4 and 4' bis[-] [(4-trifluoromethyl sulfo NIROKISHI phenyl) deca fluoro pentyl] diphenyl ether, 4 and 4' bis[-] [(3-trifluoromethyl sulfo NIROKISHI) deca fluoro pentyl] diphenyl ether, 4 and 4' bis[-] [(4-methyl sulfo NIROKISHI phenyl) tetrafluoro ethyl] diphenyl ether, 4 and 4' bis[-] [(3-methyl sulfo NIROKISHI phenyl) tetrafluoro ethyl] diphenyl ether, 4 and 4' bis[-] [(4-methyl sulfo NIROKISHI phenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(3-methyl sulfo NIROKISHI phenyl) hexafluoro propyl] diphenyl ether, 4 and 4' bis[-] [(4-methyl sulfo NIROKISHI phenyl) octafluoro butyl] diphenyl ether, 4 and 4' bis[-] [(3-methyl sulfo NIROKISHI phenyl) octafluoro butyl] diphenyl ether, - bis[(4-methyl sulfo NIROKISHI phenyl) deca fluoro pentyl] diphenyl ether, and 4 and 4 '4, 4' bis[-] [(3-methyl sulfo NIROKISHI) deca fluoro pentyl] diphenyl ether.
[0032]
[Formula 10]


-- (a2m)
(A is an electronic suction nature machine as independently defined by the formula (a1-1m) among a general formula (a2m).) B is an electron-donative atom or an electron-donative divalent radical independently, and X is a chlorine atom, a bromine atom, or an iodine atom independently. R1-R8 the same -- or -- differing -- a hydrogen atom, a fluorine atom, an allyl group, an alkyl group, or a fluoro alkyl group -- it is -- n -- two or more -- desirable -- 2-100 -- it is the integer of 2-80 especially preferably.
[0033] As the electron-donative atom or the electron-donative divalent radical (B) in the above-mentioned general formula (a2m), it is -O-, -S-, -CH=CH-, -C**C-, and [0034].
[Formula 11]


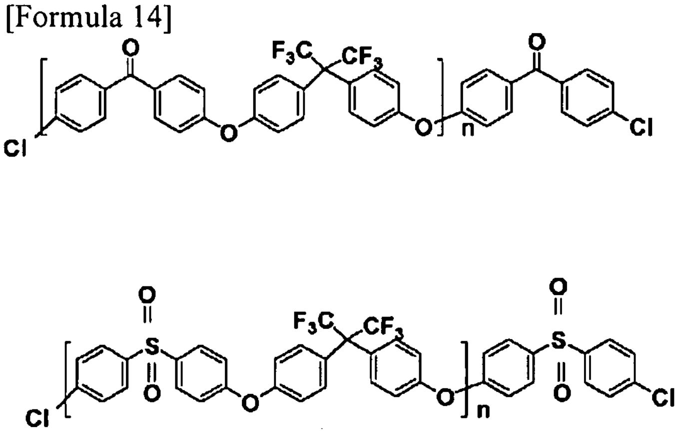
[0035]
[Formula 12]



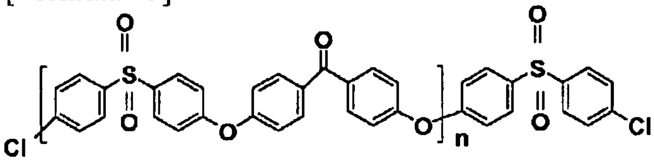
**** is mentioned.
[0036] As an example of the above-mentioned monomer (A3), a 2 and 2-screw [4-{4-(4-chloro benzoyl) phenoxy} phenyl]-1, 1, 1, 3, 3, and 3-hexafluoropropane and screw [4-{4-(4-chloro benzoyl) phenoxy} phenyl] sulfone and the thing shown with the following chemical formula are mentioned, for example.
[0037]
[Formula 13]

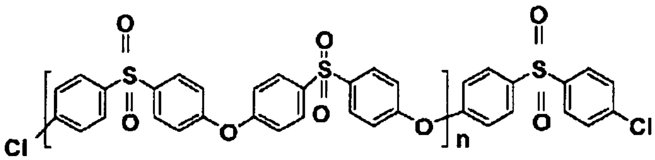


[-- X is as having defined the general formula (a2m) among the above-mentioned formula.]
[0038] As the above-mentioned monomer (A3) which can be used by this invention, n besides the monomer shown by n= 2 can use "bigger oligomer" thru/or bigger "polymer" than 2. It is as follows when the oligomer of the structure of having aromatic series chloride, or the concrete structure expression of a polymer is held at the molecule end as an example.
[0039]
[Formula 14]

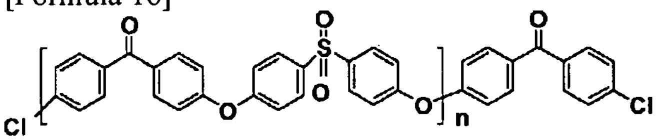


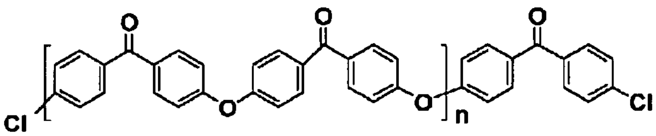
[0040]
[Formula 15]



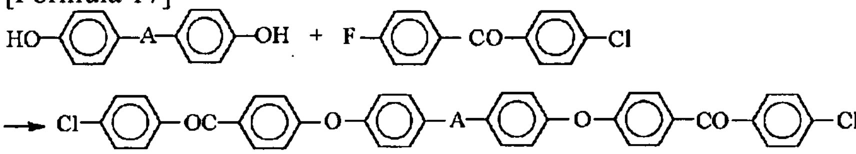


[0041]
[Formula 16]

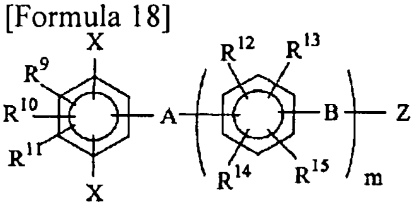




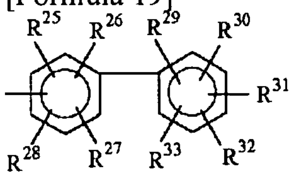
[0042] A monomer (A3) For example, the bisphenol connected with the electronic suction nature machine (A) when an electron releasing group was -O-, The aromatic series dihalide compound permuted by halogen atoms activated with the electronic suction nature machine, such as a fluorine and chlorine, For example, a - difluoro benzophenone, and 4 and 4 '4, 4'-dichloro benzophenone, 4 and 4'-chloro fluorobenzo phenon, a bis(4-chlorophenyl) sulfone, A bis(4-fluoro phenyl) sulfone, a 4-fluoro phenyl-4'-chlorophenyl sulfone, A bis(3-nitro-4-chlorophenyl) sulfone, a 2.6-dichloro benzonitrile, 2, 6-difluorobenzo nitryl, hexafluoro benzene, deca fluoro biphenyl, 2, 5-difluoro benzophenone, 1, and 3-bis(4-chloro benzoyl) benzene etc. can be made to be able to react, and it can compound. Since it is using the chloro fluoro object which it has a piece every, a fluorine atom gives priority to the halogen atom with which reactivity differs as activity aromatic series dihalide like the following reaction preferably and a phenoxide and nucleophilic substitution occur, it is convenient although the end chloro object with which the purpose was activated is acquired.
[0043]
[Formula 17]

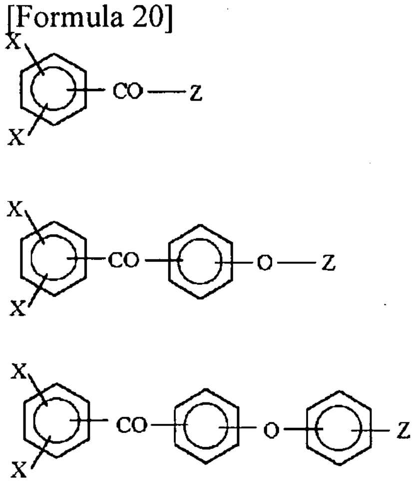


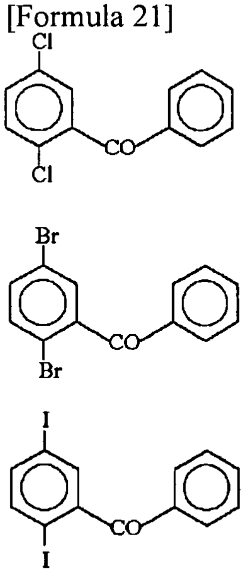
[0044] (2) As a monomer (henceforth a monomer (B)) which constitutes the monomeric unit (B) which constitutes a unit (B), the thing monomer (respectively henceforth "a monomer (B1)", "a monomer (B-2)", "a monomer (B3)", and "a monomer (B4)" in order) expressed with following general formula (b1m) - (b4m) is mentioned preferably.
[0045]
[Formula 18]



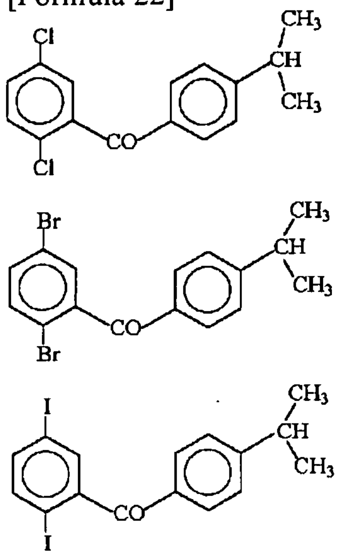
-- (b1m)

(A is an electronic suction nature machine as the formula (a1-1m) was defined among a general formula (b1m).) B is an electron-donative atom or an electron-donative radical as the formula (a2m) was defined independently, and X is a chlorine atom, a bromine atom, or an iodine atom independently. R9-R15 the same -- or it differs, and is a hydrogen atom, a fluorine atom, an allyl group, an alkyl group, or a fluoro alkyl group, Z is an aryl group, and m is the integer of 0, 1, or 2.
It is as having defined the formula (a1-1m) as the above-mentioned alkyl group or a fluoro alkyl group. Since it acts that it is the alkyl group which has the 3rd class carbon, such as an isopropyl group, as a crosslinking reaction point in the case of crosslinking reaction and the advanced crosslinked polymer electrolyte which constructed the bridge is obtained, it is desirable.
[0046] As an aryl group concerning Above Z, it is phenyl group, naphthyl group, and formula: [0047], for example.
[Formula 19]


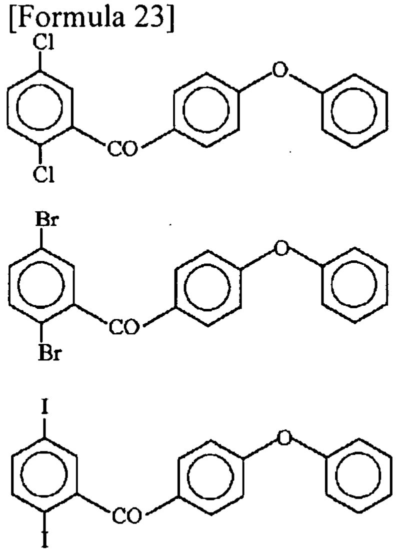
(-- R25-R33 are the same as what R9-R15 defined about the formula (b1m) among a formula.) -- the biphenylyl radical expressed is mentioned.
[0048] As a monomer (B1), the compound expressed with the following formulas is mentioned, for example.
[0049]
[Formula 20]


[-- X and Z are as having defined by the general formula (b1m) among a formula.] [0050] As an example of a monomer (B1), 2, a 4-dichloro-4'-phenoxy benzophenone, 4 '- phenoxyphenyl 2, 5-dichloro benzoate, and 4'-phenoxyphenyl 2, 4-dichloro benzoate, and the thing expressed with the following type are still more specifically mentioned.
[0051]
[Formula 21]


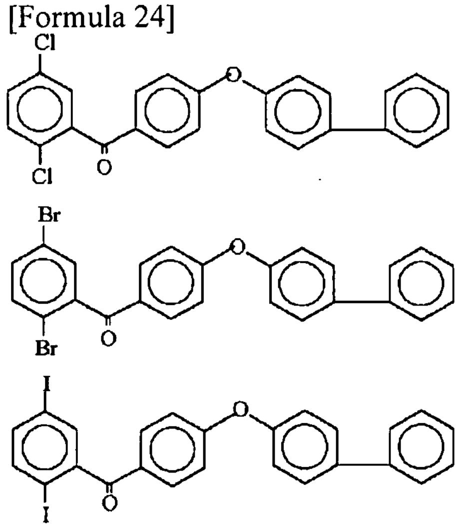
[0052]
[Formula 22]



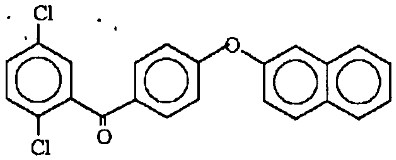
[0053]
[Formula 23]

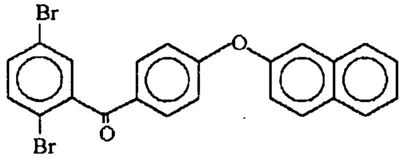


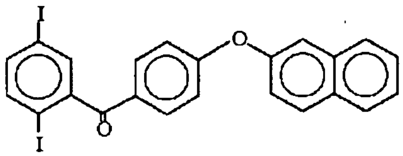
[0054]
[Formula 24]



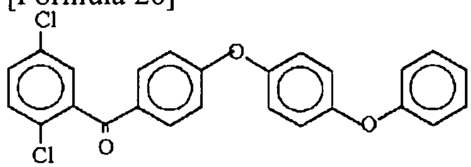
[0055]
[Formula 25]

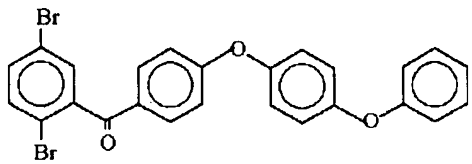


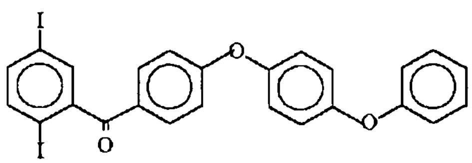




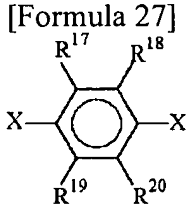
[0056]
[Formula 26]





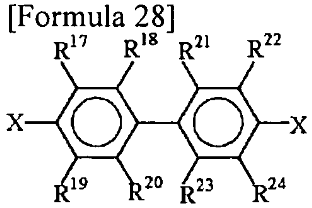


[0057] If a 2 and 5-dichloro-4'-[(4-phenoxy) phenoxy] benzophenone is taken for an example, a monomer (B1) 2 and 5-dichloro-4'-fluorobenzo phenon and p-phenoxy phenol are used as a start reaction raw material, and potassium carbonate is added to this and it changes into a reactant high phenoxide. As a reaction solvent It is compoundable using non-proton system dipole polar solvents, such as dimethylacetamide, toluene, N-methyl pyrrolidone, and dimethyl sulfoxide, etc. by making it react with the reaction temperature of 80-200 degrees C for 1 to 30 hours.
[0058]
[Formula 27]



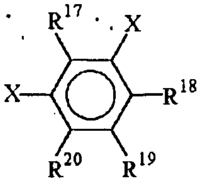
··· (b 2m)

[0059]
[Formula 28]



··· (b 3m)

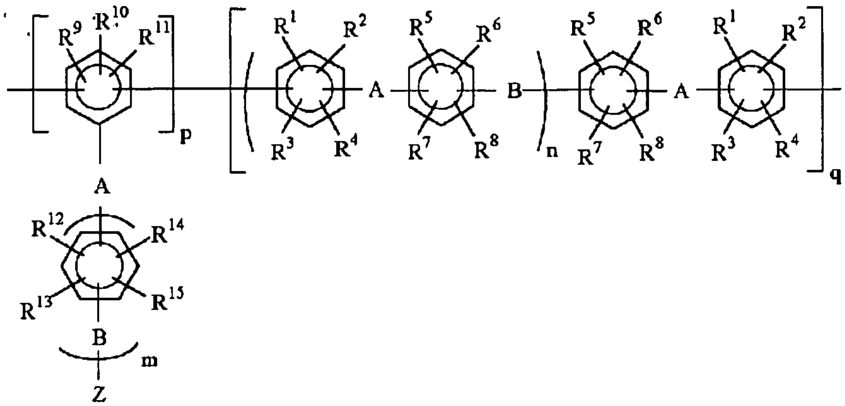
[0060]
[Formula 29]



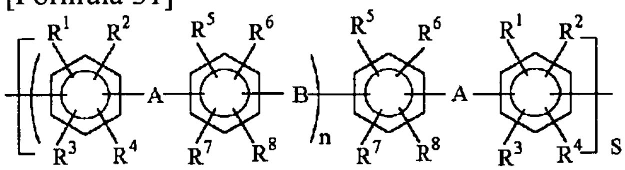
... (b 4 m)

(Into the above-mentioned general formula (b2m) (b3m) (b4m), X is a chlorine atom, a bromine atom, an iodine atom, or -OSO2Y (it is here and Y shows an alkyl group, an alkyl halide radical, or an aryl group) independently, and is that R17-R24 are the same or a difference, a hydrogen atom, a fluorine atom, an allyl group, an alkyl group, or a fluoro alkyl group.)
[0061] In general formula (b2m) - (b4m), when R17-R24 are alkyl groups, a methyl group, an ethyl group, a propyl group, butyl, a hexyl group, etc. are mentioned, and when it is a fluoro alkyl group, a truffe ROORO methyl group, a pentafluoro ethyl group, etc. are mentioned.
[0062] The following are mentioned as an example of the above-mentioned monomer (B-2). P-dichlorobenzene, p-dibromo benzene, p-diiodo benzene, p-dimethyl sulfo NIROKISHI benzene, 2, 5-dichlorotoluene, 2, 5-dibromo toluene, 2, 5-diiodo toluene, 2, 5-dimethyl sulfo NIROKISHI benzene, 2, 5-dichloro-para xylene, 2, 5-dibromo-para xylene, 2, 5-diiodo-para xylene, 2, 5-dichloro benzotrifluoride, 2, 5-dibromo benzotrifluoride, 2, 5-diiodo benzotrifluoride, 1, 4-dichloro - 2, 3, 5, 6-tetrafluoro benzene, 1, 4-dibromo - 2, 3, 5, 6-tetrafluoro benzene, 1, 4-diiodo - 2, 3, 5, 6-tetrafluoro benzene. A thing desirable also in the above is p-dichlorobenzene, p-dimethyl sulfo NIROKISHI benzene, 2, 5-dichlorotoluene, 2, and 5-dichloro benzotrifluoride.
[0063] The following are mentioned as an example of the above-mentioned monomer (B3). 4, a 4'-dimethyl sulfo NIROKISHI biphenyl, 4, 4'-dimethyl sulfo NIROKISHI -3, a 3'-dipropenyl biphenyl, 4, a 4'-dibromo biphenyl, 4, a 4'-diiodo biphenyl, 4, 4'-dimethyl sulfo NIROKISHI -3, a 3'-dimethyl biphenyl, 4, 4'-dimethyl sulfo NIROKISHI -3, a 3'-difluoro biphenyl, - dibromo octafluoro biphenyl, and - dimethyl sulfo NIROKISHI - 3, 3', and 4 and 4 '5, 5'-tetrafluoro biphenyl, 4, and 4 '4, 4'-methyl SURUFONIROKISHI octafluoro biphenyl. a thing desirable also in the above -- 4 and 4 -- a - dibromo biphenyl, and - dimethyl sulfo NIROKISHI biphenyl, 4, and 4 '4, 4'-diiodo biphenyl, and '4, 4' - dimethyl sulfo NIROKISHI -3 and 3' -- it is - dipropenyl biphenyl.
[0064] The following are mentioned as an example of the above-mentioned monomer (B4). m-dichlorobenzene, m-dibromo benzene, m-diiodo benzene, m-dimethyl sulfo NIROKISHI benzene, 2, 4-dichlorotoluene, 2, 4-dibromo toluene, 2, 4-diiodo toluene, 3, 5-dichlorotoluene, 3, 5-dibromo toluene, 3, 5-diiodo toluene, 2, 6-dichlorotoluene, 2, 6-dibromo toluene, 2, 6-diiodo toluene, 3, 5-dimethyl sulfo NIROKISHI toluene, 2, 6-dimethyl sulfo NIROKISHI toluene, 2, 4-dichloro benzotrifluoride, 2, 4-dibromo benzotrifluoride, 2, 4-diiodo benzotrifluoride, 3, 5-dichloro benzotrifluoride, 3, 5-dibromo trifluoride, 3, 5-diiodo benzotrifluoride, 1, 3-dibromo - 2, 4, 5, 6-tetrafluoro benzene. A thing desirable also in the above is m-dichlorobenzene, 2, 4-dichlorotoluene, 3, 5-dimethyl sulfo NIROKISHI toluene, 2, and 4-dichloro benzotrifluoride.
[0065] As a monomer (B) for constituting the (b) unit of the poly arylene system copolymer of this invention Also in above-mentioned monomer (B1) - (B4), from the field of solubility and macromolecule quantification Especially A dichloro benzoic-acid derivative, 2 [for example,], a 5-dichloro-4'-phenoxy benzophenone, It is desirable to use 2, 4-dichloro-4'-phenoxy benzophenone, 2, and 5-dichloro-4 '- phenoxyphenyl benzoate, 2, and 4-dichloro -4'-phenoxyphenyl benzoate.
[0066] (3) The aromatic compound unit which has an electronic suction nature machine in the synthetic (a) principal chain of the poly arylene system copolymer, (b) the poly arylene system copolymer which has the aromatic compound unit which does not have an electronic suction nature machine in a principal chain At least one sort of monomers chosen from the group which consists of the above-mentioned monomer (A1), a monomer (A2), and a monomer (A3) (A), It is compoundable with a coupling reaction with at least one sort of monomers (B) chosen from the group which consists of the above-mentioned monomer (B1), a monomer (B-2), a monomer (B3), and a monomer (B4).
[0067] It is a catalyst system containing a transition-metals compound, and as this catalyst system, the catalyst used in case the poly arylene system copolymer is manufactured uses as an indispensable component the compound (henceforth a ligand component) used as (1) transition-metals salt and a ligand or the transition metal complex (copper salt is included) with which coordination of the ligand was carried out, and (2) reducing agents, and further, in order to gather a rate of polymerization, it may add a "salt."
[0068] here -- as a transition-metals salt -- nickel compounds, such as a nickel chloride, nickel bromide, nickel iodide, and nickel acetylacetonato, a palladium chloride, and bromination -- cobalt compounds, such as iron compounds, such as palladium compounds, such as palladium and iodation palladium, ferric chloride, iron bromide, and iron iodide, a cobalt chloride, a cobalt bromide, and a cobalt iodide, etc. are mentioned. A nickel chloride, nickel bromide, etc. are [especially among these] desirable.

[0069] Moreover, as a ligand component, although a triphenyl phosphine, 2, 2'-bipyridine, 1, 5-cyclo-octadiene, 1, and 3-bis(diphenyl phosphino) propane etc. is mentioned, triphenyl phosphine, 2, and a 2'-bipyridine are desirable. The compound which is the above-mentioned ligand component is one-sort independent, or can use two or more sorts together.
[0070] furthermore, as a transition metal complex with which coordination of the ligand was carried out beforehand For example, a nickel chloride screw (triphenyl phosphine), a nickel bromide screw (triphenyl phosphine), A nickel iodide screw (triphenyl phosphine), a nickel nitrate screw (triphenyl phosphine), A nickel chloride (2 and 2'-bipyridine), nickel bromide (2 and 2'-bipyridine), Nickel iodide (2 and 2'-bipyridine), nickel nitrate (2 and 2'-bipyridine), Although bis(1, 5-cyclo-octadiene) nickel, tetrakis (triphenyl phosphine) nickel, tetrakis (triphenyl phosphite) nickel, tetrakis (triphenyl phosphine) palladium, etc. are mentioned A nickel chloride screw (triphenyl phosphine) and a nickel chloride (2 and 2'-bipyridine) are desirable.
[0071] Although iron, zinc, manganese, aluminum, magnesium, sodium, calcium, etc. are mentioned and the thing of them can be carried out, for example as the above-mentioned reducing agent which can be used for the above-mentioned catalyst system, zinc, magnesium, and manganese are desirable. By making acids, such as an organic acid, contact, these reducing agents can be activated more and can be used.
[0072] moreover, as a "salt" which can be used in a catalyst system A sodium fluoride, a sodium chloride, a sodium bromide, a sodium iodide, Sodium compounds, such as a sodium sulfate, a potassium fluoride, potassium chloride, Potassium compounds, such as a potassium bromide, potassium iodide, and potassium sulfate, Although ammonium compounds, such as tetraethylammonium fluoride, a tetraethylammonium chloride, a tetraethylammonium bromide, iodation tetraethylammonium, and sulfuric-acid tetraethylammonium, etc. are mentioned A sodium bromide, a sodium iodide, a potassium bromide, a tetraethylammonium bromide, and iodation tetraethylammonium are desirable.
[0073] A transition-metals salt or 0.0001-10 mols of transition metal complexes of the operating rate of each component in a catalyst system are usually 0.01-0.5 mols preferably to a total of one mol of the above-mentioned monomer. In less than 0.0001 mols, when a polymerization reaction does not fully advance but exceeds ten mols on the other hand, there is a problem that molecular weight falls.
[0074] In a catalyst system, when using a transition-metals salt and a ligand component, 0.1-100 mols of operating rates of this ligand component are usually 1-10 mols preferably to one mol of transition-metals salts. In less than 0.1 mols, catalytic activity becomes inadequate, and on the other hand, when it exceeds 100 mols, there is a problem that molecular weight falls.
[0075] Moreover, 0.1-100 mols of operating rates of the reducing agent in a catalyst system are usually 1-10 mols preferably to a total of one mol of the above-mentioned monomer. In less than 0.1 mols, when a polymerization does not advance enough but exceeds 100 mols on the other hand, there is a problem that purification of the polymer obtained becomes difficult.
[0076] Furthermore, when using a "salt" for a catalyst system, 0.001-100 mols of the operating rate are usually 0.01-1 mol preferably to a total of one mol of the above-mentioned monomer. Less than 0.001 mols of the effectiveness of gathering a rate of polymerization are insufficient, and on the other hand, when it exceeds 100 mols, there is a problem that purification of the polymer obtained becomes difficult.
[0077] As a polymerization solvent which can be used for composition of the poly arylene system copolymer, for example, a tetrahydrofuran, a cyclohexanone, dimethyl sulfoxide, N.N-dimethylformamide, N,N-dimethylacetamide, a N-methyl-2-pyrrolidone, gamma-butyrolactone, gamma-butyrolactam, etc. are mentioned, and a tetrahydrofuran, N.N-dimethylformamide, N,N-dimethylacetamide, and a N-methyl-2-pyrrolidone are desirable. As for these polymerization solvents, using, after fully drying is desirable. The concentration of the grand total of the above-mentioned monomer in a polymerization solvent is usually 5 - 40 % of the weight preferably one to 90% of the weight.
[0078] Moreover, 0-200 degrees C of polymerization temperature at the time of carrying out the polymerization of the poly arylene system copolymer are usually 50-120 degrees C preferably. Moreover, polymerization time amount is usually 1 - 40 hours preferably for 0.5 to 100 hours.
[0079] Here, it is general formula: [0080] by carrying out a polymerization on condition that the above using a monomer (A3) and a monomer (B1).
[Formula 30]



(-- here, A, B, Z, R1-R15, and m and n are as above-mentioned, p and q show the number of each repeating units independently, and the ratios (namely, mole ratio of the two above-mentioned repeating units) of p/q are 99 / 1 - 20/80.) -- the copolymer expressed is obtained.
[0081] The structure of the poly arylene system copolymer can be checked by the infrared absorption spectrum by C-O-C absorption of 1,230-1,250cm-1, C=O absorption of 1,640-1,660cm-1, etc., and can check the structure from the peak of a 6.8-8.0 ppm aromatic series proton with a nuclear-magnetic-resonance spectrum (1 H-NMR).
[0082] (4) The poly arylene system polymer of the following structure expression (A) is compoundable with the same approach and conditions as the case of the synthetic above-mentioned poly arylene system copolymer of the poly arylene system polymer, using a monomer (A3) as a raw material.
[0083]
[Formula 31]



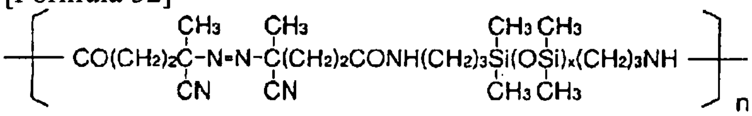
-- (A) (here, A, B, Z, R1-R8, and n are as above-mentioned, and s shows the number of repeating units.)
[0084] (5) Sulfonation of the poly arylene system (**) polymer, next the polymer which has a sulfonic group (**) can use a sulfonation agent for the above-mentioned (**) polymer which does not have a sulfonic group, and can obtain it by introducing a sulfonic group with a conventional method.
[0085] As an approach of introducing a sulfonic group, the copolymer which does not have the above-mentioned sulfonic group can be sulfonated on well-known conditions under a non-solvent or solvent existence using well-known sulfonation agents, such as a sulfuric anhydride, an oleum, a chlorosulfonic acid, a sulfuric acid, and a sodium hydrogensulfite, for example.
[0086] As a solvent, halogenated hydrocarbon, such as tetrachloroethane besides ethers solvents, such as hydrocarbon solvents, such as n-hexane, a tetrahydrofuran, and dioxane, dimethylacetamide, dimethylformamide, and non-proton system polar solvents like dimethyl sulfoxide, a dichloroethane, chloroform, and a methylene chloride, etc. is mentioned, for example. Although especially a limit does not have reaction temperature, -50-200 degrees C is usually -10-100 degrees C preferably. Moreover, reaction time is usually 1 - 200 hours preferably for 0.5 to 1,000 hours.
[0087] thus, the amount of sulfonic groups in the sulfonic group content (**) polymer of this invention obtained -- 0.5 - 3 milliequivalant /g -- they are 0.8 - 2.8 milliequivalant /g preferably. By under 0.5 milliequivalant / g, if proton conductivity does not go up but 3 milliequivalant / g is exceeded on the other hand, a hydrophilic property will improve, and it will become a water-soluble polymer, or will not result in water solubility, but endurance will fall [**].
[0088] The above-mentioned amount of sulfonic groups can be easily adjusted the operating rate of a monomer (A) and a monomer (B), and by changing the class of a monomer (A) and monomer (B), and combination further.
[0089] moreover, the molecular weight of the polymer of the precursor before sulfonation of the sulfonic group content poly arylene system (**) polymer obtained by doing in this way -- polystyrene equivalent weight average molecular weight -- it is -- 10x103 to 1,000x103 -- it is 20x103 to 800x103 preferably. As for paint film nature, less than 10x103 are [that a crack occurs etc.] insufficient for a shaping film, and there is a problem also in an intensive property. On the other hand, when 1,000x103 is exceeded, there are problems, like

solubility becomes inadequate, and solution viscosity is high and workability becomes a defect.
[0090] In addition, the structure of a sulfonic group content poly arylene system (**) polymer can be checked by the infrared absorption spectrum by S=O absorption of 1,030-1,045cm-1 and 1,160-1,190cm-1, C-O-C absorption of 1,130-1,250cm-1, C=O absorption of 1,640-1,660cm-1, etc., and these presentation ratios can be known by the neutralization titration of a sulfonic acid, and elemental analysis. Moreover, the structure can be checked from the peak of a 6.8-8.0 ppm aromatic series proton with a nuclear-magnetic-resonance spectrum (1 H-NMR).
[0091] Moreover, the water of organic acids, such as inorganic acids, such as a sulfuric acid and a phosphoric acid, and a carboxylic acid, and optimum dose etc. may be used together with the sulfonic group content (**) polymer concerning this invention.
[0092] 2. [the polymerization of the cross-linking monomer under existence of a proton conductivity polymer] By carrying out the radical polymerization reaction of the cross-linking monomer under existence of a proton conductivity polymer, the crosslinked polymer electrolyte concerning this invention can be obtained. the operating rate of a proton conductivity polymer and a cross-linking monomer -- 99.9 - 50 / 0.1-50-fold quantitative ratio -- desirable -- It is 99.9-70/30. [0.1-30]
[0093] It is more desirable to make a cross-linking monomer react to the bottom of existence of the radical polymerization initiator which generates a radical according to an operation of heat, light, or a reducing agent as a polymerization reaction.
[0094] As this radical polymerization initiator, organic peroxide and an azobis system radical polymerization initiator are mentioned. If organic peroxide is used, since crosslinking reaction will advance more, it is desirable.
[0095] As an example of organic peroxide, it is (1). Diacyl peroxide, such as acetyl peroxide, benzoyl peroxide, ISOBUCHI roil peroxide, 2,4-dichlorobenzyl peroxide, 3 and 5, 5-trimethylhexanoyl peroxide, octanoyl par OKISAODO, lauroyl peroxide, stearoyl peroxide, succinic acid peroxide, and m-toluoyl benzoyl peroxide;
[0096] (2) Ketone peroxides, such as methyl ethyl ketone peroxide, cyclohexanon peroxide, methylcyclohexanone peroxide, and acetylacetone peroxide;
[0097] (3) Hydroperoxide, such as a hydrogen peroxide, t-butyl hydroperoxide, a cumene hydroperoxide, p-menthonaphtene hydroperoxide, diisopropylbenzene hydroperoxide, 1, 1 and 3, 3-tetramethyl BUCHIRUHAIDORO peroxide, and t-hexyl hydroperoxide;
[0098] (4) Dialkyl peroxide, such as di-t-butyl peroxide, dicumyl peroxide, dilauryl peroxide, alpha, and alpha'-bis(tert-butyl peroxide) JIISOPUROPIRUBEN, 2, the 5-dimethyl -2, a 5-bis(tert-butyl peroxide) hexane, t-butyl cumyl peroxide, 2, the 5-dimethyl -2, and 5-bis(tert-butyl peroxide) hexyne -3;
[0099] (5) T-butyl peroxyacetate, t-butylperoxy perpivalate, t-hexyl peroxy pivalate, 1, 1 and 3, and 3-tetramethyl butylperoxy 2-ethylhexanoate, 2, the 5-dimethyl -2, a 5-bis(2-ethyl hexa noil peroxy) hexane, 1-cyclohexyl-1-methylethyl peroxy 2-ethylhexanoate, t-hexyl peroxy 2-ethylhexanoate, t-butylperoxy2-ethylhexanoate, T-buthylperoxy isobuthylate, t-hexyl peroxy isopropyl MONOKABONETO, Tert-butyl peroxide isopropyl mono-carbonate, tert-butyl peroxide 2-ethylhexyl mono-carbonate, t-BUCHIRUPAOKI sialyl mono-carbonate, t-butyl par OKISHIMAREETO, T-butylperoxy-3,5,5-trimethyl hexanoate, t-butyl peroxy laurate, 2, the 5-dimethyl -2, a 5-bis(m-toluoyl peroxy) hexane, alpha and alpha'-bis(neo decanoyl peroxy) diisopropylbenzene, Cumil peroxy neodecanoate, 1, 1 and 3, 3-tetramethyl butylperoxyneodecanoate, 1-cyclohexyl-1-methylethyl peroxy neo decanoate, T-hexylperoxy neodecanoate, t-butyl par OKISHINEODO decanoate, T-butyl peroxybenzoate, t-hexyl peroxy benzoate, Bis(tert-butyl peroxide) isophthalate, 2, the 5-dimethyl -2, a 5-bis(benzoylperoxy) hexane, Peroxy ester, such as tert-butyl peroxide m-toluoyl benzoate, 3, 3', 4, and a 4'-tetrapod (tert-butyl peroxide carbonyl) benzophenone;
[0100] (6) The 1 and 1-screws (t-hexyl peroxy) 3 and 3, a 5-trimethyl cyclohexane, The 1 and 1-bis(t-hexyl peroxy) cyclohexane, 1, and 1-screws (tert-butyl peroxide) 3 and 3, a 5-trimethyl cyclohexane, A 1 and 1-bis (tert-butyl peroxide) cyclohexane, 1, and 1-bis(tert-butyl peroxide) cyclo dodecane, Peroxy ketals, such as a 2 and 2-bis(tert-butyl peroxide) butane, n-butyl 4, 4-bis(tert-butyl peroxide) valerate, 2, and 2-bis(4 and 4-G t-butylperoxycyclohexyl) propane;
[0101] (7) Peroxi dicarbonate, such as di-n-propyl peroxi dicarbonate, JISOPURO pill peroxi dicarbonate, bis (4-t-butyl cyclohexyl) peroxi dicarbonate, di-2-ethoxyethylperoxydicarbonate, di-2-ethylhexylperoxycarbonate, di-2-methoxybutylperoxydicarbonate, and JI (3-methyl-3-methoxy butyl) peroxi dicarbonate, other t-butyl trimethylsilyl peroxide, etc. are mentioned.
[0102] As an example of an azobis system radical polymerization initiator Azobisisobutyronitril, azobisiso valeronitrile, 2, and 2'-azobis (4-methoxy-2,4-dimethylvaleronitrile), - azobis (2,4-dimethylvaleronitrile), and 2 and 2 '2, 2'-azobis (2-methyl butyronitrile), 1 and 1'-azobis (cyclohexane-1-carbonitrile), 2-(carbamoylazo)-isobuthylonitryl, 2 and 2'-azobis [a 2-methyl-N-{1 and 1-bis(hydroxymethyl)-2-hydroxyethyl} propione amide],

2 and 2'-azobis [2-methyl-N-{2-(1-hydroxy butyl)} propione amide], 2 and 2'-azobis [a 2-methyl-N-(2-hydroxyethyl)-propione amide], 2 and 2'-azobis [an N-(2-propenyl)-2-methyl propione amide], 2 and 2'-azobis (N-butyl-2-methyl propione amide), 2 and 2'-azobis (N-cyclohexyl-2-methyl propione amide), 2 and 2' azobis [-] [2-(5-methyl-2-imidazoline-2-IRU) propane] dihydrochloride, 2 and 2' azobis [-] [2-(2-imidazoline-2-IRU) propane] dihydrochloride, 2 and 2'-azobis [2-(2-imidazoline-2-IRU) propane] JISARUFETO JIHAIDO rate, 2 and 2' azobis [-] [2-(3, 4, 5, 6-tetrahydro pyrimidine-2-IRU) propane] dihydrochloride, 2 and 2' azobis [-] [2-{1-(2-hydroxyethyl)-2-imidazoline-2-IRU} propane] dihydrochloride, 2 and 2'-azobis [2-(2-imidazoline-2-IRU) propane], 2 and 2'-azobis (2-methyl propione amidine) dihydrochloride, 2 and 2'-azobis [an N-(2-carboxy ethyl)-2-methyl-propione amidine], 2, 2 '- azobis (2-methyl propione amidoximes) and dimethyl 2 and 2'-azobis butyrate, The polymer expressed with 4,4'-azobis(4-cyanopentanoic acid), 2, and 2'-azobis (2, 4, and 4-trimethyl pentane) and the following type is mentioned.

[0103]

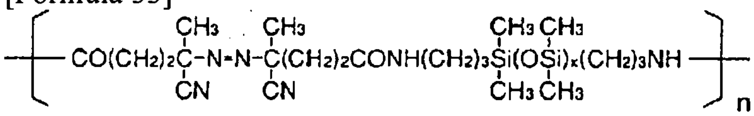
[Formula 32]



(Molecular weight: About 30,000-40,000)

[0104]

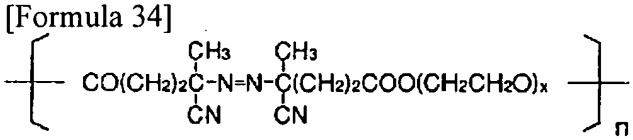
[Formula 33]



(Molecular weight: About 70,000-90,000)

[0105]

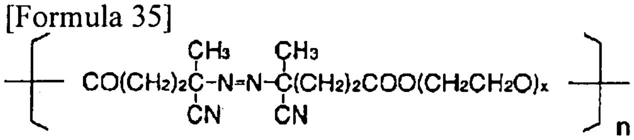
[Formula 34]



(Molecular weight: About 15,000-30,000)

[0106]

[Formula 35]

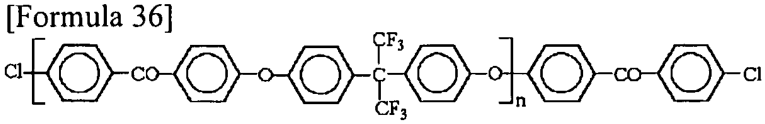


(Molecular weight: About 25,000-40,000) In addition, persulfate, such as ammonium persulfate, sodium persulfate, and potassium persulfate, can be used as a radical polymerization initiator.

[0107] The number of the polymerization nature machines of the monomer which has two or more radical polymerization nature machines in 1 molecule is 5 thru/or 6 especially preferably four or more still more preferably three or more preferably. As a monomer which has two or more radical polymerization nature machines in 1 molecule For example, dipentaerythritol hexa (meta) acrylate, dipentaerythritol PENTA (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, pen TAERISURITORUTORI (meta) acrylate, Ethylene GURIKORUJI (meta) acrylate, tetra-ethylene GURIKORUJI (meta) acrylate, Polyethylene GURIKORUJI (meta) acrylate, 1, 4-butane JIORUJI (meta) acrylate, To 1 and 6-, KISANJIORUJI (meta) acrylate, neopentyl GURIKORUJI (meta) acrylate, Trimethylol propane TORIOKISHI ethyl (meta) acrylate, tris (2-hydroxy ethyl) iso SHIANURETOTORI (meta) acrylate, Tris (2-hydroxyethyl) iso SHIANURETOJI (meta) acrylate, Bis (hydroxymethyl) tricyclo DEKANJI (meta) acrylate, The di(meth)acrylate of the diol which is the adduct of the ethyleneoxide of bisphenol A, or propylene oxide, The di(meth)acrylate of the diol which is the adduct of the ethyleneoxide of hydrogenation bisphenol A, or propylene oxide, The epoxy (meta) acrylate which made hydroxyalkyl (meta) acrylate, such as hydroxy (meta) acrylate, add to the diglycidyl ether of bisphenol A, The di(meth)acrylate of polyoxyalkylene-ized bisphenol A, p- or m-divinylbenzene, triethylene glycol divinyl ether, etc. are mentioned.

[0108] As a commercial item of the monomer which has two or more radical polymerization nature machines in 1 molecule For example, KAYARAD-DPHA, KAYARAD R-604, DPCA-20, -30, -60, -120, HX-620, D-310,

D-330 (above) YUPIMA [ ] UV by Nippon Kayaku Co., Ltd. -- SA1002 and SA2007 (above) The Mitsubishi Chemical make, bis-coat #195, #230, #215, #260, #335H.P., # 295, #300, #700 (OSAKA ORGANIC CHEMICAL INDUSTRY, LTD. make), light acrylate 4 EG-A, 9 EG-A, NP-A, DCP-A, BP-4EA, BP-4PA, PE-3A, PE-4A, DPE-6A (above, product made from Kyoeisha Chemistry), ARONIKKUSU M-208, M-210, M-215, M-220, M-240, M-305, M-309, M-315, M-325 (above, Toagosei make), etc. are mentioned.
[0109] What is necessary is just to carry out a radical polymerization and crosslinking reaction at temperature higher than after that in the manufacture approach of the crosslinked polymer electrolyte concerning this invention, while heating it after fabricating by casting what mixed the polyfunctional radical polymerization nature monomer and the radical polymerization initiator in the shape of a film and vaporizing a solvent, after dissolving a sulfonic group content copolymer in a solvent in order to obtain an electrolyte membrane (proton conduction film) for example. The obtained bridge formation film is an insoluble thru/or poorly soluble thing, and can already be used for a solvent as an electrolyte membrane (proton conduction film).
[0110] As a solvent in the above and the casting method, non-proton system polar solvents, such as dimethylacetamide, dimethylformamide, a N-methyl-2-pyrrolidone, and dimethyl sulfoxide, etc. are mentioned. Alcohols solvents, such as a methanol, may be further mixed by these solvents.
[0111] The crosslinked polymer electrolyte obtained by the manufacture approach of this invention is available as a filmy body on the proton conductivity film available to for example, the electrolyte for primary cells, the electrolyte for rechargeable batteries, the giant-molecule solid electrolyte for fuel cells, a display device, various sensors, a signal transduction medium, a solid-state capacitor, ion exchange membrane, etc.
[0112]
[Example] Although an example is given and this invention is explained still more concretely hereafter, this invention is not limited to the following examples.
[0113] In addition, it asked for various kinds of parameters in an example as follows.
The weight average molecular weight of the precursor polymer before [weight-average-molecular-weight] sulfonation used the tetrahydrofuran (THF) for the solvent, and calculated the molecular weight of polystyrene conversion with gel permeation chromatography (GPC).
[0114] It washed until the rinsing water of the sulfonation polymer [amount of a sulfonic group] Obtained was set to pH 4-6, and after removing a free extant acid, it fully rinsed, weighing capacity of the specified quantity was carried out after desiccation, it dissolved in the partially aromatic solvent of THF/water, the phenolphthalein was used as the indicator, it titrated with the standard solution of NaOH, and the amount (milliequivalant/g) of a sulfonic group was calculated from the point of neutralization.
[0115] The film-like sample with a diameter of 13mm put on the bottom of [measurement of proton conductivity] 100% relative humidity was inserted into the platinum electrode, and was enclosed with the sealing cel, and the absolute value and phase angle of an impedance of a cel were measured using the impedance analyzer (HYP4192A) at the frequency of 5-13MHz, the applied voltage of 12mV, the temperature of 20 degrees C, 50 degrees C, and 100 degrees C. The obtained data performed complex impedance measurement in oscillation level 12mV using the computer, and computed proton conductivity.
[0116] [Measurement of tensile strength, hauling ductility, and Young's modulus] tensile strength, hauling ductility, and Young's modulus were measured by the tension test in the room temperature of the obtained film.
[0117] [Fenton trial] The Fenton's reagent was prepared so that the concentration of iron ion might be set to 20 ppm to 3% of the weight of a hydrogen peroxide in an iron sulfate and 7 hydrate. Extracted the 200g Fenton's reagent in the 250 cc solution made from polyethylene, the 45-degree C constant temperature bath was made immersed after [after throwing in the macromolecule electrolysis film cut to 3cmx4cm and thickness =55micrometer] sealing, and the 150h Fenton trial was performed. The film was taken out after the Fenton trial, ion exchange water performed 25 degree C, 50%RH, and 12h condition preparation after rinsing, and various physical-properties measurement was performed. The weight retention in the Fenton trial was computed with the following formula.
Film weight x100[0118] before the film weight / Fenton trial after the weight retention (%) = Fenton trial in the Fenton trial - Synthetic] of the synthetic example 1-[sulfonation polymer 1
An agitator, a thermometer, a cooling pipe, Dean-Stark tubing, (Composition of oligomer) To the flask of 3 openings of 1L which attached the three-way cock of nitrogen installation, it is 2 and 2-screw (4-hydroxyphenyl). - 1, 1, 1, 3, 3, 3 - Hexafluoropropane (bisphenol A F) 67.3g (0.20 mols), 4 and 4'-dichloro benzophenone (4 and 4'-DCBP) 60.3g (0.24 mols), Potassium carbonate 71.9g (0.52 mols), N,N-dimethylacetamide (DMAc) 300mL, and toluene 150mL are taken, and it heats all over an oil bath and under nitrogen-gas-atmosphere mind, and is under churning. It was made to react at 130 degrees C. Azeotropy of the water generated by the reaction is carried out to toluene, and if it is made to react while Dean-Stark tubing removes out of a system, generation of water will no longer be accepted hardly in about 3 hours. Reaction

temperature It raised from 130 degrees C to 150 degrees C gradually. Then, after removing a great portion of toluene and continuing a reaction by 150 ** for 10 hours, raising reaction temperature to 150 degrees C gradually, 4 and 4'-DCBP 10.0g (0.040 mols) was added, and it reacted for further 5 hours. Filtration removal of the precipitate of the inorganic compound which carried out the byproduction was carried out after cooling the obtained reaction mixture radiationally, and filtrate was thrown in in the methanol of 4L. The products which precipitated are collected a ** exception and they are after desiccation and a tetrahydrofuran. It dissolved in 300mL. This was reprecipitated to methanol 4L and 95g (85% of yield) of the target compounds was obtained.
[0119] The number average molecular weight of the polystyrene conversion for which it asked by GPC (THF solvent) of the obtained polymer was 4,200, and weight average molecular weight was 8,300. Moreover, the obtained polymer was meltable to THF, NMP, DMAc, a sulfolane, etc., Tg was 110 degrees C and pyrolysis temperature was 498 degrees C.
[0120] The obtained oligomer is formula (I): [0121].
[Formula 36]


-- It is presumed that it has the structure expressed with (I), and it is the average of n, in view of this structure and the above-mentioned number average molecular weight. It asked with 7.8.
[0122] (Composition of the poly arylene system copolymer) The desiccation nitrogen purge of oligomer [of said formula (I)]g [28.4] (2.87mmol) and 2 and 5-dichloro-4'-(4-phenoxy) phenoxy benzophenone (DCPPB) 29.2g (67.1mmol), bis(triphenyl phosphine) nickel dichloride 1.37g (2.1mmol), iodine sodium 1.36g (9.07mmol), triphenyl phosphine 7.34g (28.0mmol), and the 11.0g (168mmol) of the zinc dust was carried out for the flask. N-methyl pyrrolidone (NMP) 130ml was added, and it heated at 80 degrees C, and stirred for 4 hours, and the polymerization was performed. The polymerization solution was diluted with THF, coagulation recovery was carried out with the hydrochloric acid/methanol, methanol washing was repeated, the vacuum drying of the polymer by reprecipitation which refined and carried out the ** collection was carried out to the dissolution and a methanol by THF, and 50.7g (96%) of the target copolymers was obtained. The number average molecular weight of the polystyrene conversion for which it asked by GPC (THF) was 40,000, and weight average molecular weight was 145,000.
[0123] (Preparation of the sulfonation polymer 1) 25g of copolymers obtained above was put into the 500ml separable flask, 250ml of sulfuric acids was added 96%, and it stirred under the nitrogen air current for 24 hours. The obtained solution was poured out into a lot of ion exchange water, and the polymer was settled. Washing of a polymer was repeated until pH of wash water became neutrality. It dried and the 29g (96%) sulfonation polymer was obtained. The sulfonation equivalents of a sulfonation polymer were 1.70 milliequivalant /g.
[0124] - Synthetic] of the synthetic example 2-[sulfonation polymer 2
2, 5-dichloro-4'-phenoxy benzophenone 193.5g (540mmol), 4 and 4'-dichloro benzophenone 15.1g (60mmol), 11.7g (78mmol) of sodium iodides, Bis-triphenyl phosphine nickel dichloride 11.8g (1.8mmol), Triphenyl phosphine 63.0g (240mmol) and 94.1g (1.44 mols) of zinc Ring current tubing, It put into the three necked flask which attached the three-way cock, and attached to the 70-degree C oil bath, and, in addition to [1,000ml of N-methyl-2-pyrrolidones] the bottom of nitrogen-gas-atmosphere mind, the reaction was started after the nitrogen purge. It diluted with 500ml of N-methyl-2-pyrrolidones after the 20-hour reaction, 1:10 hydrochloric acids / methanol solution was filled with polymerization reaction mixture, and white powder was obtained for the polymer after filtration and a vacuum drying after a deposit and washing. Yield was 153g. Moreover, weight average molecular weight was 159,000. The obtained polymer was produced using the N-methyl-2-pyrrolidone, and swelling was not observed although immersed into the methanol.
[0125] To polymer 150g obtained the account of a top, 1,500ml of concentrated sulfuric acid was added, at the room temperature, it stirred and the sulfonation reaction was performed for 24 hours. It poured after a reaction and into a lot of pure water, and the sulfonation polymer was deposited. Backwashing by water of a polymer was continued until it was set to pH7, sulfonation polymers were collected after filtration, and the vacuum drying was carried out at 90 degrees C. The yield of a sulfonation polymer was 179g. The sulfonation equivalents of a sulfonation polymer were 2.45 milliequivalant /g.
[0126] - The mixture (trade name: KAYARAD-DPHA (Nippon Kayaku Co., Ltd. make)) 10 weight section of dipentaerythritol hexaacrylate and dipentaerythritol pentaacrylate and the peroxide (di-t-butyl peroxide) 1 section were mixed as the 10%NMP solution 900 weight section (amount of sulfonation polymer 1 solid content 90 weight section) of the sulfonation polymer 1 obtained in the example 1 of the example 1-above-mentioned composition, and a cross-linking monomer, and the uniform NMP solution was adjusted.

[0127] After applying this NMP solution by the thickness of 55 micrometers on a glass substrate using a doctor blade, predrying was carried out for 1 hour using oven at 70 degrees C, and the paint film was removed from the glass substrate. The film was heat-treated at 170 more degrees C after fixing on an aluminum plate on the heat-resistant tape for 1 hour, and the crosslinked polymer electrolysis film which performs the polymerization and crosslinking reaction of a cross-linking monomer, and is made into the purpose was obtained. Subsequently, in order to remove completely NMP which remains in a paint film, you made it immersed for seven days at a room temperature into distilled water, and Survival NMP was removed. Then, film desiccation was performed.

[0128] When the insoluble matter to N-methyl pyrrolidone (NMP) was measured about this film-like crosslinked polymer electrolyte, it is 95 % of the weight, and it turned out that it is the film of the structure where the bridge is constructed by altitude. Various physical-properties measurement was performed for the film after 25 degree C and 50%RH 12-hour condition preparation. A result is shown in Table 1. The film concerned was what maintains high proton conductivity and high tensile strength, and is extremely excellent in physical-properties balance before and after the Fenton trial, without carrying out film degradation.

[0129] - In the example of comparison 1-above-mentioned example 1, **** for the 100 weight sections and a film were obtained for the sulfonation polymer 1 without performing a polymerization and bridge formation. Various physical-properties measurement results are shown in Table 1.

[0130] - In the example 2-example 1, it replaced with the sulfonation polymer 1 and the film-like crosslinked polymer electrolyte was obtained like the example 1 except using the sulfonation polymer 2 which was obtained in the synthetic example 2 and to carry out. Various physical-properties measurement results are shown in Table 1.

[0131] - In the example of comparison 2-above-mentioned example 2, **** for the 100 weight sections and a film were obtained for the sulfonation polymer 2 without performing a polymerization and bridge formation. Various physical-properties measurement results are shown in Table 1.

[0132]

[Table 1]

[実施例・比較例]

		実施例1	実施例2	比較例1	比較例2
ポリマー成分	スルホン化ポリマー1(重量部)	90		100	
	スルホン化ポリマー2(重量部)		90		100
モノマー	KAYARAD-DPHA(日本化薬製)(重量部)	10	10	−	−
重合開始剤	ジ−t−ブチルパーオキサイド(重量部)	1	1	−	−

[耐久試験データ]

		実施例1	実施例2	比較例1	比較例2
フェントン試験前(架橋反応後)	重量保持率(%)	100	100	100	100
	NMP不溶部(%)	95	96	0	0
	イオン交換容量	1.7	2.43	2.33	2.41
	プロトン伝導度(S/cm)at85℃、90%RH	0.145	0.176	0.173	0.175
	重量平均分子量	276000	487000	458000	471000
	数平均分子量	67000	75200	74500	77300
	ヤング率(MPa)	2510	3250	3050	3080
	引っ張り強度(MPa)	67	102	88	89
	引っ張り伸び(%)	45	5.1	4.7	5.5
フェントン試験後	重量保持率(%)	97	100	0	0
	NMP不溶部(%)	93	92	塗膜溶解のため測定不能。	塗膜溶解のため測定不能。
	イオン交換容量	1.7	2.45		
	プロトン伝導度(S/cm)at85℃、90%RH	0.147	0.176		
	重量平均分子量	274000	482000		
	数平均分子量	65800	74900		
	ヤング率(MPa)	2490	3160		
	引っ張り強度(MPa)	68	92		
	引っ張り伸び(%)	55	5.1		

[0133]

[Effect of the Invention] According to this invention, it became possible to offer the crosslinked polymer electrolyte which maintains the high proton conductivity originally needed, and is extremely excellent in endurance. And since the bridge is constructed over the proton conductivity polymer by altitude by the cross-linking monomer, this crosslinked polymer electrolyte can be especially used suitably as proton conduction film of the fuel cell of high endurance. Moreover, this thing is available as conduction film, such as the electrolyte for primary cells, the electrolyte for rechargeable batteries, a display device, various sensors, a signal transduction medium, a solid-state capacitor, and ion exchange membrane, and this industrial meaning is size very much.